DIVERGENCE OF THE QUASIPARTICLE LIFETIME WITH DOPING AND EVIDENCE FOR PRE-FORMED PAIRS BELOW T* IN $YBa_2Cu_3O_{7-\delta}$: Direct measurements by femtosecond time-resolved spectroscopy.

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We report new time-resolved data of quasiparticle relaxation and Cooper pair recombination dynamics in $YBa_2Cu_3O_{7-\delta}$, measured as a function of temperature and doping δ using femtosecond optical spectroscopy. The data show the existence of a normal state pseudo-gap for in-plane charge excitations below T^* and an unusual divergence of the quasiparticle relaxation time in the superconducting state τ_s with δ towards optimum doping. In the underdoped state, no change in the amplitude of the induced transmission (which is proportional to the DOS at E_F), or relaxation time τ_s is observed at T_c. From the sum rule, both observations signify that no gap opens at T_c in underdoped YBCO for $\delta > 0.15$. T_c in this case only signifies the onset of phase coherence. The presented data thus suggest pair formation with an associated redistribution of the DOS starting at T^* and the establishment of phase coherence at T_c consistent with Bose-Einstein condensation. In the optimally doped material, $\delta \approx 0.1$, on the other hand, both a divergence in lifetime and a change of the DOS occur at T_c, signifying the opening of a gap and the occurence of pairing takes place simultaneously.

I. INTRODUCTION

The low-energy electronic excitation spectrum in high-temperature superconducting cuprates has been controversial ever since the first experimental data were reported on the subject more than 10 years ago. The standard measurement techniques used to obtain experimental data have been mainly infrared reflectivity, transmission and ellipsometry together with electronic Raman scattering. Although there was significant agreement regarding the raw data between different groups[1], controversy arose when interpretation of the spectra was attempted. The single particle spectrum on the other hand was very successfully investigated by angle-resolved photoemission (ARPES)[2]. However in this case, just as for optical spectroscopy, the complexity of the observed multi-component spectral features necessitates the use of a model in interpreting the data. Furthermore in all time-integrated spectroscopies the issue of whether the spectrum shows homogeneous or inhomogeneous linewidth cannot be easily circumvented, so particle lifetimes determined by these techniques are necessarily ambiguous.

In this paper we describe an example of the application of time-resolved optical spectroscopy to the direct investigation of low-energy electronic excitation dynamics. The method by default directly gives quasiparticle lifetimes in the case of high-temperature superconductor materials. From such measurements as a function of temperature and doping δ in $YBa_2Cu_3O_{1-\delta}$ we are able to infer the occurrence of Bose-Einstein condensation of quasiparticles at T_c in the underdoped state and a cross-over to BCS-like state near optimum doping.

II. EXPERIMENTS

The success of the time-resolved spectroscopy method relies on two factors. Firstly the technological developments of femtosecond lasers and related technology, with the recent development of high-frequency lock-in amplifiers. Secondly - a particularly important generic feature of the cuprate materials - the existence of a charge-transfer resonance in the wavelength region of 800 nm easily accessible by these lasers. The assignment of this resonance by use of laser wavelengths ranging from 1500 to 350 nm has been particularly important for the understanding the time-resolved measurements[3]. In previous work[4,5], the spectroscopy off-resonance (usually at 2 eV) showed features which were substantially more difficult to interpret.

The laser used in the present time-resolved experiment was a Ti:Sapphire mode-locked laser giving 150 fs pulses at 800 nm with a repetition rate of 88 MHz. The pump pulse train average power was typically between 10 and 120 mW, while the probe pulse train was typically 0.2 mW or less. The two beams were focussed onto the sample mounted onto a copper block in an Oxford Instruments Microstat. The pump beam was modulated at 200 kHz and the probe detected via an amplified photodiode and a high-frequency digital lock-in amplifier (EG&G 7260).

For the understanding of the present experiments, it is important to establish that the optical transitions involve excitations from the ground state (of predominantly O character) near E_F to unoccupied states (of predominantly Cu orbitals) 1.5 eV above in energy. In such a resonance case, the changes in the ground state DOS occurring with temperature, particularly at T_c and T^* can thus be measured by pump-probe spectroscopy. The evidence for the assignment given above is summarized below. From early X-ray work of Bianconi and others[6] it emerged that the charge carriers (holes) are located mainly on the O ions, while the Cu d (upper Hubbard) band is approximately 1.5-1.8 eV higher in energy (depending on the material and level of doping). Experiments on $YBa_2Cu_3O_x$ for example have shown that the charge transfer (CT) transition between O and Cu is strongly observed in optical conductivity, optical ellipsometry[7] and absorption spectra[8] as well as photoconductivity[8] at 1.8 eV with a typical width of 0.1 eV. Upon doping it splits into two bands approximately ~ 0.1 eV apart at the insulator-to metal transition[7,9] and eventually at optimum doping only a peak at 1.5 eV is clearly visible. A feature at 1.5 eV is clearly observed also in large-shift electronic Raman scattering[10]with an apparent splitting observed at $\delta \sim 0.6$. This probably indicates that the local symmetry for the CT transition is lower than orthorhombic and has no center of inversion, otherwise the 1.5 eV feature would not be seen both in *gerade* (Raman) and *ungerade* (infrared) transitions.

Further confirmation that the initial states for optical excitations at 1.5 eV cross E_F comes from thermal differential reflectance (TDR)[11] and time-resolved (TR) optical spectroscopies[3]. The former measures the change in reflectivity which occurs at T_c as a result of the redistribution of the DOS and shows distinctly a double peak at 1.5 eV similar to the one seen in the optical conductivity and Raman spectra. TR spectroscopy shows the same feature at 1.5 eV in the optimally doped $YBa_2Cu_3O_{7-\delta}$ - albeit with much lower resolution - also appearing below T_c[3] and is similarly thought to be caused by a redistribution of initial states for the optical transitions at E_F. In this case the $4:1$ in-plane to out-of-plane polarization ratio also confirms this assignment. Yet more independent confirmation that the initial states for absorption are at E_F come from ARPES[2] in conjunction with theoretical calculations, while the effect of doped holes on the 1.5 eV transition was nicely demonstrated by Matsuda et al[12].

The schematic diagram for the resonant pump and probe processes which is based on the assignment discussed above is shown in Figure 1. The carriers are first excited by the pump pulse from occupied states at or below E_F. The second, probing step involves determining - as a function of time - the resulting changes in the density of states at E_F $N(0)$, caused by the photoexcited quasiparticles by measuring the change in transmission $\mathcal{T}$ of the sample with a delayed weak laser probe pulse. In the adiabatic approximation, the golden rule gives the *change* in optical absorbance of the probe pulse to be proportional to the change in the DOS at E_F i.e. $\delta A \propto \delta N(0)$ caused by the pump pulse. Since - as was discussed above - this is in turn proportional to $N(0)$, the time-resolved changes in optical transmission $\delta\mathcal{T}/\mathcal{T}\,(=-\delta\mathcal{A}/\mathcal{A})$ can directly probe temperature- and δ- dependence of $N(0)$. The probe pulse was polarized in the $a-b$ plane to probe predominantly CuO-plane excitations (the signal was found previously to be independent of pump polarization[3]).

III. EXPERIMENTAL RESULTS

The induced transmission $\Delta\mathcal{T}/\mathcal{T}$ following the pump pulse typically shows a relatively fast relaxation of $\tau \sim 0.5$ - 3 ps, followed by a distinct long-lived component with a decay time 10 ns or more[3,13], which is most evident in optimally doped YBCO with $x = 6.94$ and also for $x \sim 6.75$. This long lived component is attributed to quasiparticle relaxation in localized states and was discussed in detail by Stevens et al[3]. In this paper we will only discuss the fast component of the relaxation. The amplitude of this component was measured *well below* T_c as a function of doping x in YBCO over a wide range of doping. The results shown in Figure 2 indicate that the integrated amplitude - which is proportional to the total number of particles excited, $n = \int(dn/dt)dt \propto \int_{-\infty}^{5\tau} \delta\mathcal{T}/\mathcal{T}\,dt$ - increases almost linearly with doping, starting at the insulator-to-metal transition at $x = 6.4$. (Near optimum doping, the non-integrated amplitude of the signal actually decreases, but this is not attributed to a drop in the DOS, but rather to the fact that the relaxation time τ starts to increase dramatically for $x \to 6.9$.)

An important feature of the data is that the amplitude is strongly temperature dependent (Figure 3). At low temperatures ($T < T_c$) the amplitude is nearly temperature independent. With increasing temperature the amplitude starts to drop and eventually vanishes, such that at room temperature the signal is usually not visible, or very small. The temperature T^* at which the amplitude $\delta\mathcal{T}/\mathcal{T}$ drops to zero - indicating a change (drop) in the DOS at E_F - increases with decreasing carrier concentration in the underdoped phase in close agreement with the "pseudogap" temperatures for YBCO determined from other experiments[14]. Importantly, near optimum doping the amplitude vanishes near T_c, which has already been noted previously[3]. In underdoped samples on the other hand, the amplitude shows *no change* at T_c, suggesting no changes in the DOS take place at T_c, which as we shall discuss below is presented as evidence for Bose-Einstein condensation.

As already mentioned briefly above, the quasiparticle lifetime τ_s in the superconducting state - determined by fitting a single exponential to the time resolved trace - shows a divergence with increasing carrier concentration $1-\delta$, in the region close to optimum doping as shown in Figure 4. In contrast, almost no change in lifetime with δ is observed above T_c, and is $\tau_n = 0.5 \pm 0.1$ ps at 100 K over the whole range of doping. Importantly, the lifetimes below and above T_c in the underdoped state are typically the same below $x \sim 6.85$. Approaching optimum doping, this is no longer the case, and a clear divergence of τ is observed at T_c, behavior which is well known in BCS superconductors[15] and is thought to be due to a quasiparticle relaxation bottleneck as $T \to T_c$ from below (not a Hebel-Slichter peak).

IV. DISCUSSION

The systematic investigation of the amplitude and relaxation time τ of the photoinduced optical transmission through thin film samples shows rather well the cross-over in behavior which occurs near optimum doping. In the underdoped state, neither the amplitude (which is related to the DOS at E_F) nor the lifetime τ show any effect at T_c. Instead, both show a gradual change with temperature, the amplitude vanishing at T^*, while the lifetime showing only very gradual change up to T^*. The simplest way to explain the behavior in the underdoped state is to assume that no change in amplitude or relaxation time is observed at T_c because no change in DOS (i.e. gap) occurs at T_c. Instead - in a typical Bose-Einstein scenario - the pairs which are formed at T^* only acquire phase coherence at T_c.

The onset of a macroscopically coherent condensed state occurs when the wavefunctions of adjacent pairs overlap sufficiently for phase coherence to be established between them. We can estimate the temperature at which the phase coherence is established by considering when the DeBroglie wavelength λ becomes comparable to the superconducting coherence length ξ. Thus $k_B T_c \simeq \hbar^2/(m^*\xi^2)$, which, using measured values of $\xi = 18$ A for YBaCuO[16] and $m^* = 3m_e$, gives $T_c = 91$ K, which is close to the observed T_c-s in this material. The density of carriers at the point of condensation

is given by Einstein[17] as $(N/V)^{2/3} = 2.612^{-2/3} m^* k_B T_c / 2\pi\hbar^2$ which, using the same value of m^* and T_c as above, gives $n_c = N/V \sim 10^{21} cm^{-3}$ which is close to the value estimated from Hall data[16].

The data in the near-optimally doped material with $x > 6.85$ are distinctly different to the undedoped state. Both the amplitude and the relaxation time show a dramatic change at T_c, the latter exhibiting diverging behavior as T approaches T_c similar to BCS superconductors like Al[18]. The amplitude on the other hand shows a rapid drop to zero very close to T_c, also with a BCS-like T-dependence, suggesting that a gap opens simultaneously with pair formation (and phase coherence) as in the BCS case.

To conclude, time-resolved optical spectroscopy is demonstrated to be a powerful tool for the investigation of quasiparticle dynamics in HTS. The occurrence of BE condensation in underdoped YBCO - as suggested by the absence of any observable change in the quasiparticle relaxation time τ or density of states $N(0)$ at T_c in our experiments - is consistent with simple theoretical expectations. Obeyance of the sum rule implies that pairs must form above T_c (the observed changes in the DOS from $\Delta\mathcal{T}/\mathcal{T}$ suggest that this occurs at T^*). In contrast, the optimally doped and overdoped state appears to show a divergence in the quasiparticle lifetime with doping and a BCS-like temperature dependence of both the intensity and lifetime is also apparent.

V. FIGURE CAPTIONS

Figure 1. A schematic diagram of the pump and probe processes in resonance with the 1.5 eV CT transition in YBaCuO. The carriers relax rapidly to a quasi-steady state between the pump and the probe pulses.

Figure 2. The amplitude of the induced transmission (squares) increases with doping, following T_c. The data for T_c are from Conder et al[19].

Figure 3. The temperature dependence of the amplitude of the induced transmission for a number of different samples. The T_c-s are shown in the plot. The temperature at which $\Delta T/T$ drops to zero is close to the pseudogap temperature T^*.

Figure 4. The relaxation time measured as a function of doping in the normal state at 100 K (top panel) and at 20 K (lower panel). A clear divergence of τ_s^{20K} is observed near optimum doping.

VI. ACKNOWLEDGMENTS

We wish to acknowledge V.V.Kabanov for useful discussions and T.Mertelj for his comments regarding the present manuscript.

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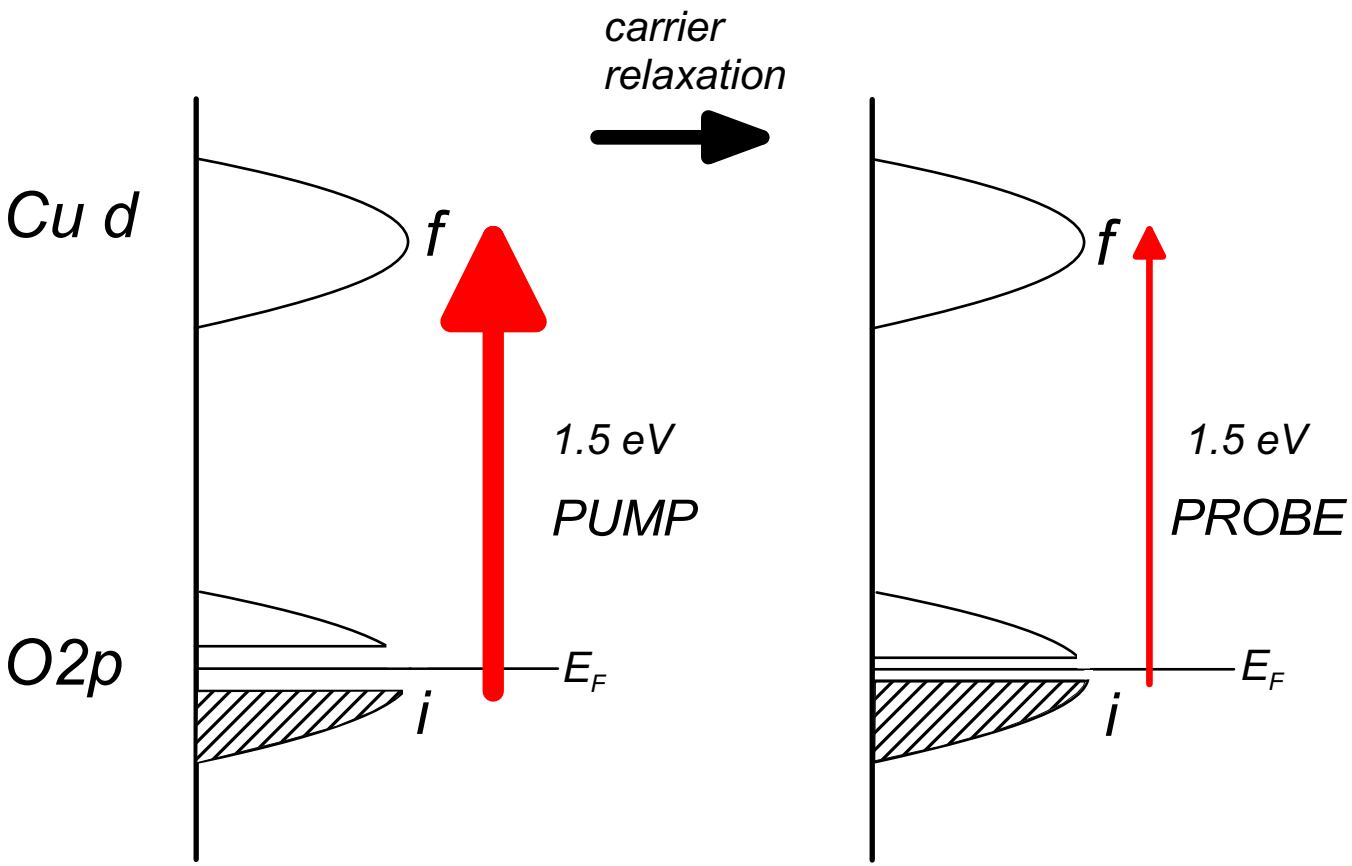
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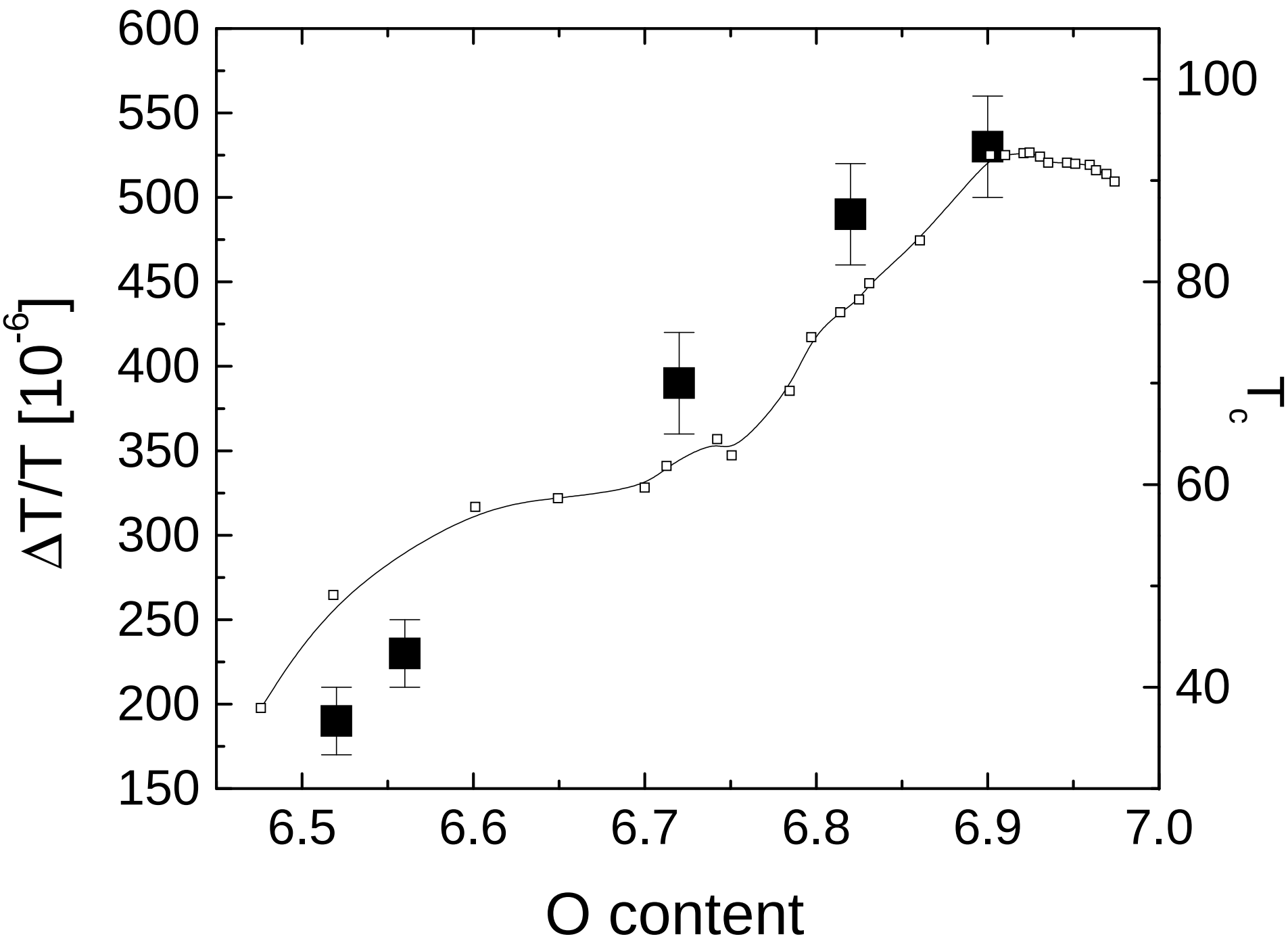
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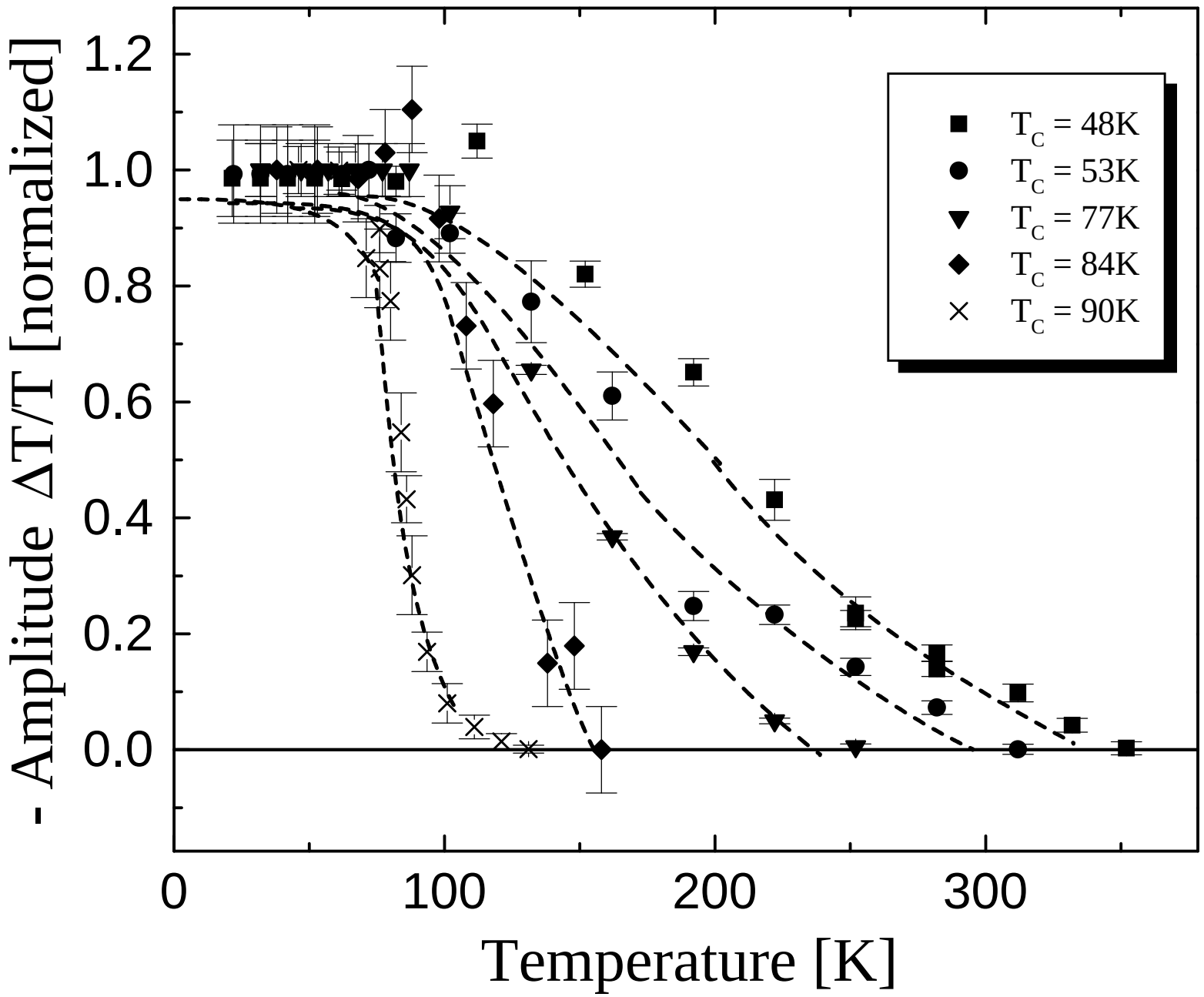
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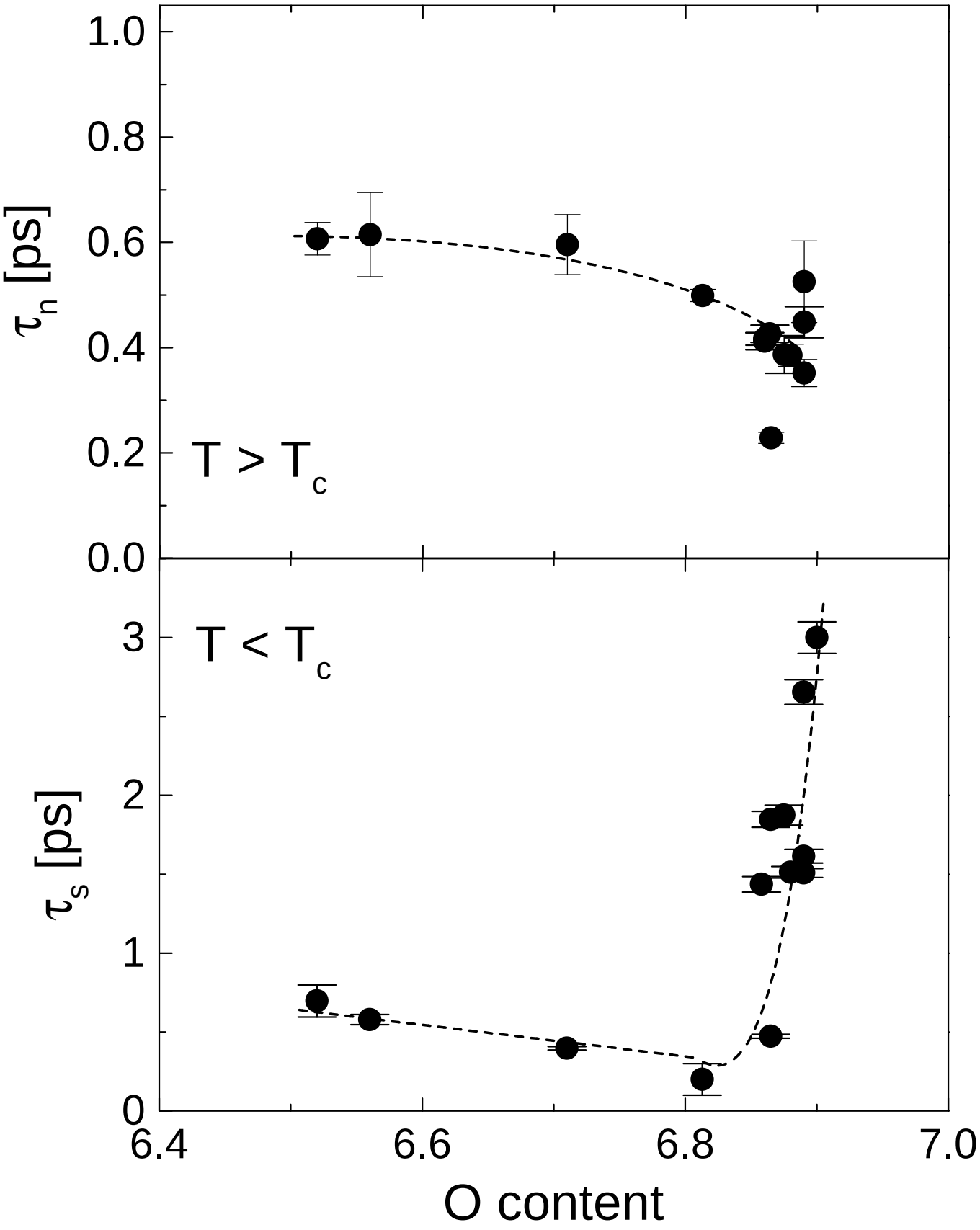
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